Development of Passive HC/NOx Trap Catalysts for Low Temperature Gasoline Applications

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Project ID #:
ace130

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Overview

Timeline

- Project start date: 9/1/17
- Project end date: 8/31/20 (now 11/30/20)
- Percent complete: 49%

Budget

- Total project funding
  - DOE share: $2,098,350
  - Contractor share: $300,614
- Funding for FY 2018: $845,015
- Funding for FY 2019: $743,731

Barriers and Technical Targets

- Barriers addressed:
  - Improve low temperature and cold start NOx control
  - Improve low temperature and cold start HC control
  - Characterize and understand Passive NOx Adsorber (PNA) durability

Partners

- Collaboration: Ford, ORNL, Purdue, UC Berkeley, BASF
- Project lead: U. Kentucky

Relevance

Impact

- Improved Pd/zeolite HC/NOx adsorbers will enable vehicle manufacturers to satisfy future emission standards and improve vehicle fuel economy by reducing cold start fueling requirements

Objectives

- Fundamental understanding of the chemistry of NOx adsorption and reduction in Pd/zeolites will be attained
- Pd/zeolites will be tailored with respect to performance and durability for application as HC/NOx adsorbers
- HC/NOx adsorber performance will be validated using exhaust gas from an engine dynamometer
- Scientific insights and technology will be transferred to the automotive industry via the project's industry partners

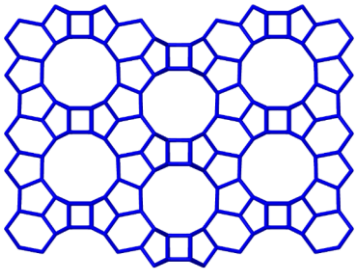
While this technology should be applicable to both gasoline and diesel vehicles, gasoline applications are emphasized in this project, given the importance of stoichiometric engines in the U.S. automotive market

Milestones

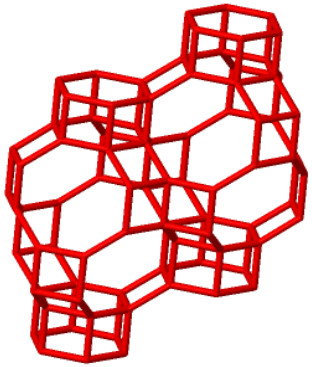
Task	Date	FY2018 Milestone Description	Status
Catalyst synthesis	-	Synthesis of large (10 g) batches of Pd/zeolites to distribute to the entire team as baseline catalysts	Done
Catalyst characterization	8/31/18	Elucidation of the structure of Pd^{2+} cations exchanged into CHA and BEA	Done/on-going
Reactor studies (Go/no-go)	-	NO adsorption capacity of degreened Pd/CHA and Pd/BEA superior to Pd/CeO_2-ZrO_2 benchmark in stoichiometric exhaust (<100 °C).	Done

Task	Date	FY2019 Milestone Description	Status
Spectroscopic studies	2/28/19	Role of alkyl nitrite and isocyanate species in NO-C_2H_4 and NO-CO co-adsorption delineated	Done/on-going
Computational study	5/31/19	Structure and IR spectra of NO, C_2H_4, and $CH_3C_6H_5$ adsorbed on Pd^{2+} cations in CHA defined	Done/on-going
Computational study	8/31/19	Structure and IR spectra of NO, C_2H_4, and $CH_3C_6H_5$ adsorbed on Pd^{2+} cations in BEA defined	Done/on-going
Catalyst synthesis	11/30/19	Baseline Pd-CHA and Pd-BEA monolith catalysts prepared	To be done
Catalyst synthesis (Go/no-go)	11/30/19	Synthesis of Pd/zeolite catalyst (> 20 g) of optimized composition and structure	To be done

Approach



Beta (BEA)



Chabazite (CHA)

- Use combination of experimental and computational methods to allow a deeper understanding of the governing chemistry in Pd-zeolite PNAs
- Pd-CHA as (relatively!) simple system amenable to study, Pd-Beta as commercially relevant system
- Focus in Years 1 and 2 on understanding how framework type, SAR, Al distribution, etc., impact NO adsorption and desorption behavior
- Focus in Year 3 on design of optimized system and assessment of durability

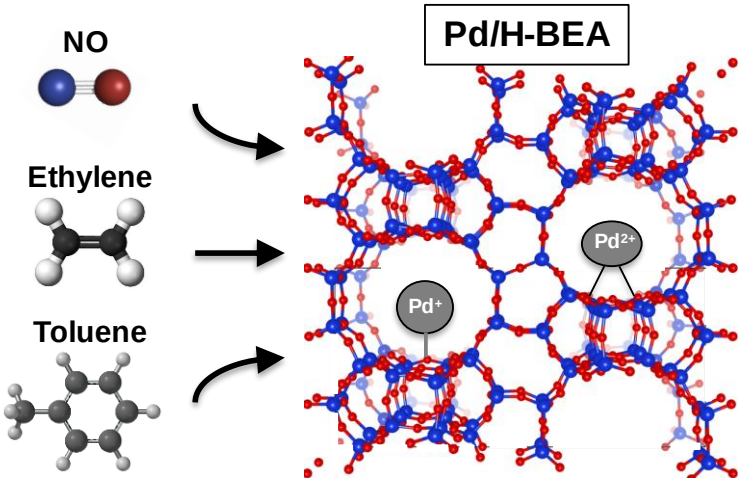
Collaboration

- **UK** (Mark Crocker):
  Project management, spectroscopic studies (DRIFTS, ESR, XPS), catalyst aging
- **Purdue** (Raj Gounder):
  Zeolite/catalyst synthesis, catalyst characterization, spectroscopic studies (XAS)
- **UC Berkeley** (Alex Bell):
  NOx/HC adsorption/desorption and kinetic studies, computational studies
- **Ford** (Christine Lambert):
  NOx/HC adsorption/desorption studies, catalyst evaluation, emissions modeling
- **ORNL** (Vitaly Prikhodko):
  Catalyst characterization (TEM), catalyst aging, catalyst evaluation (slip stream from engine test bench)
- **BASF** (Xinyi Wei):
  Catalyst preparation (monoliths)

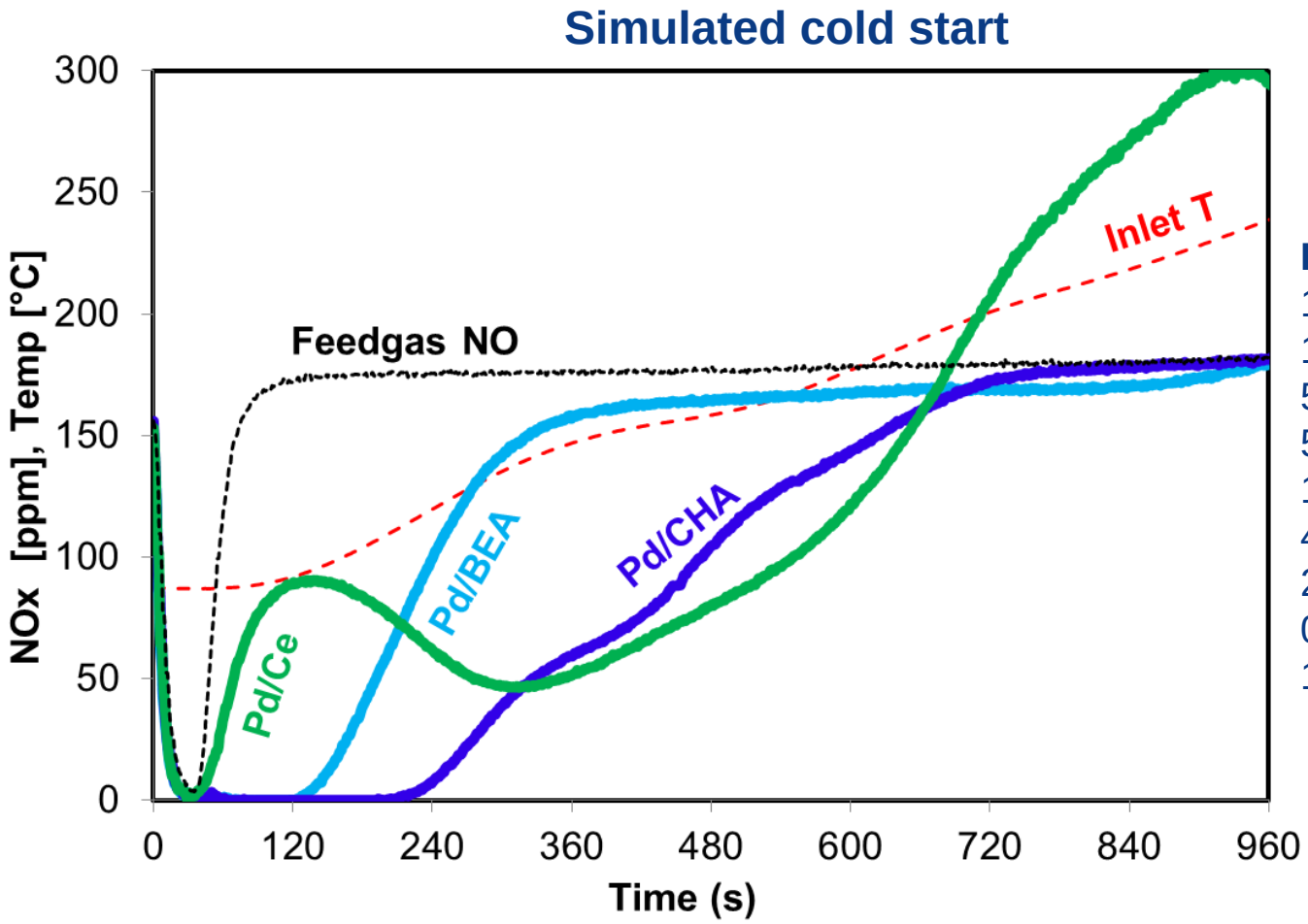
Technical Accomplishments

Work focused in five main areas to date:

- Pd-CHA and Pd-Beta synthesis and characterization
- Microreactor studies of NO adsorption and desorption
- Pd-CHA evaluation in simulated cold start tests
- DRIFTS studies to characterize Pd speciation and NO adsorption sites
- Computational studies to characterize Pd speciation and NO adsorption sites



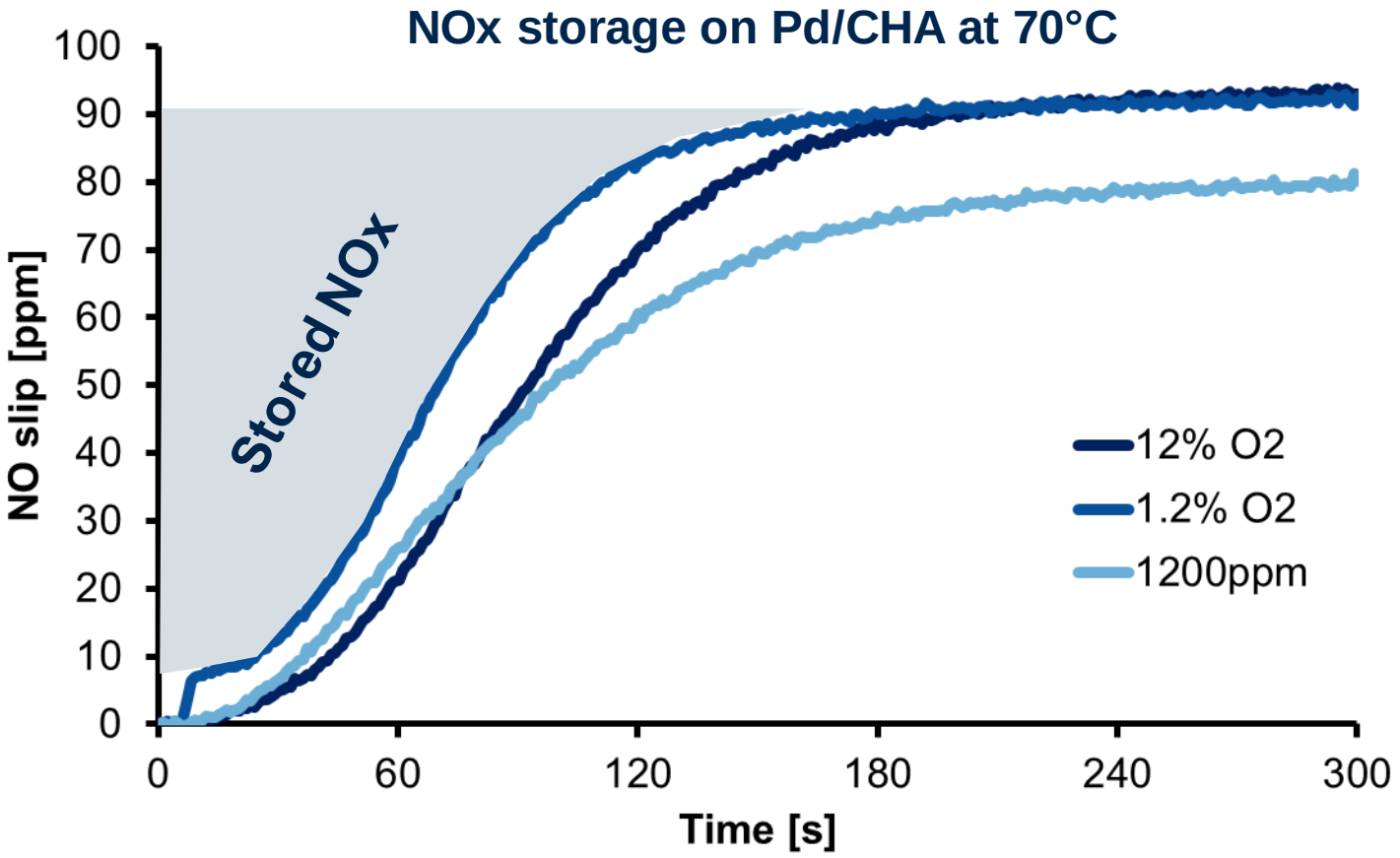
Comparing PNA Technologies (lean)



Ramp from 90°C
170 ppm NO
10% O_2
5% H_2O
5% CO_2
1350 ppm CO
450 ppm H_2
250 ppm C_2H_4
0.8 g powder
1.2 L/min total flow

Pd/CHA has higher storage efficiency than Pd/BEA or Pd/CeO_x

From Lean to Stoichiometric Feed



Lean

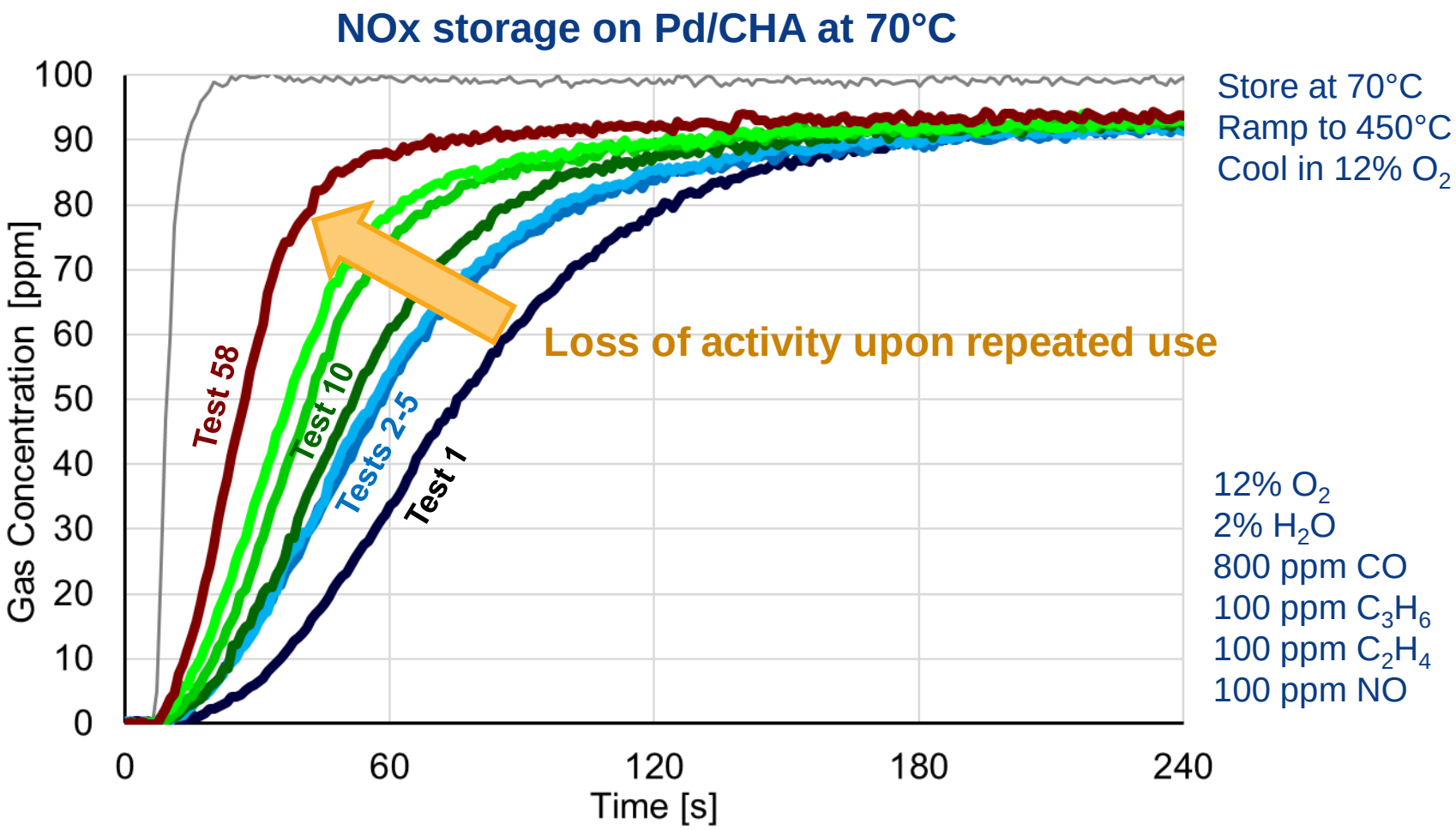
Stoichiometric

Clean-out at 600°C in 12% O_2 before each test

0.12 – 12% O_2
2% H_2O
800 ppm CO
100 ppm C_3H_6
100 ppm C_2H_4
100 ppm NO

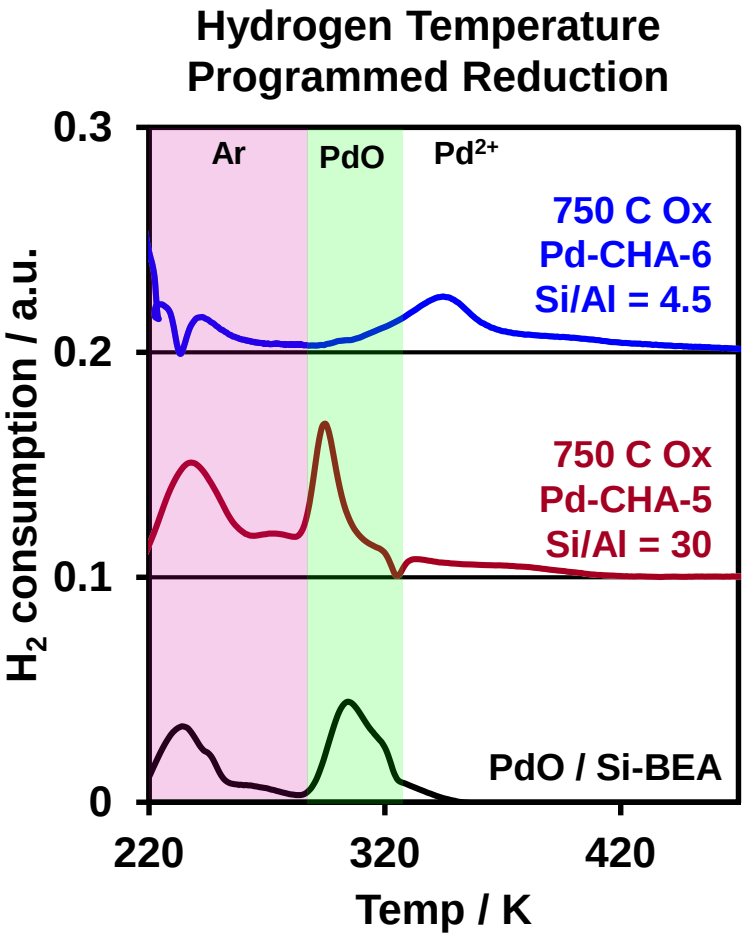
Oxygen level exerts only a relatively minor effect on NOx storage behavior

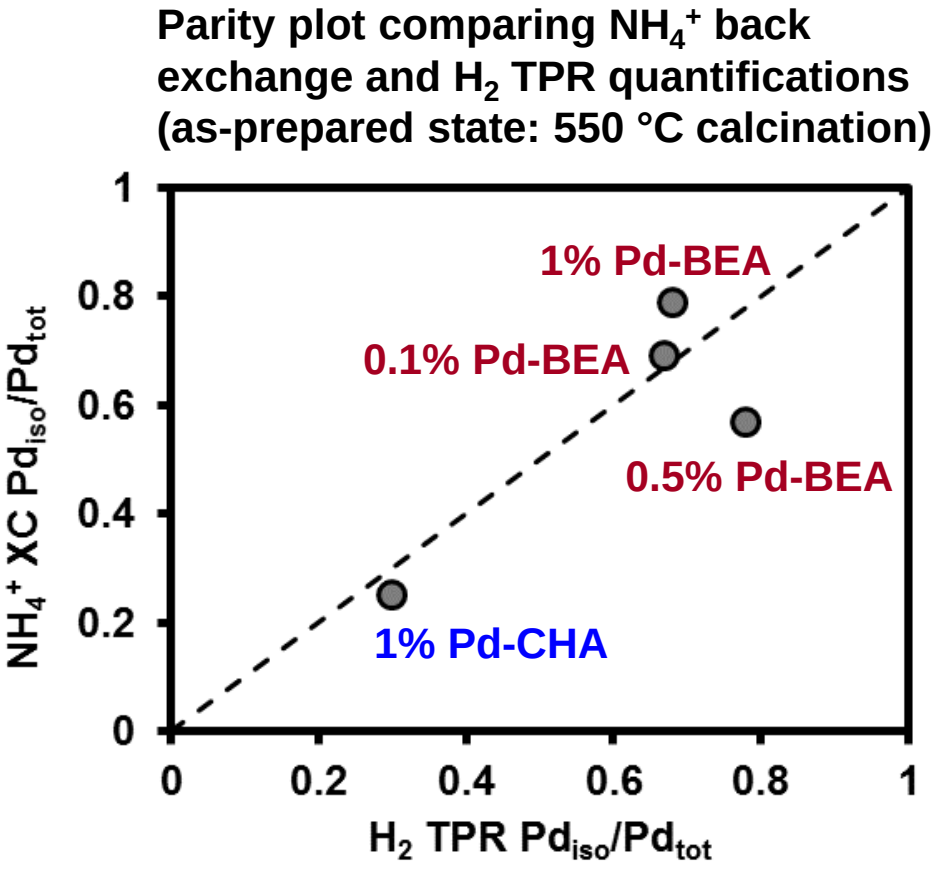
Impact of Repeated Cycling



Initially stable performance deteriorates substantially upon extended cycling; stability improvements are required for technology to be commercially viable

Characterization of Pd Species in Zeolites for PNA

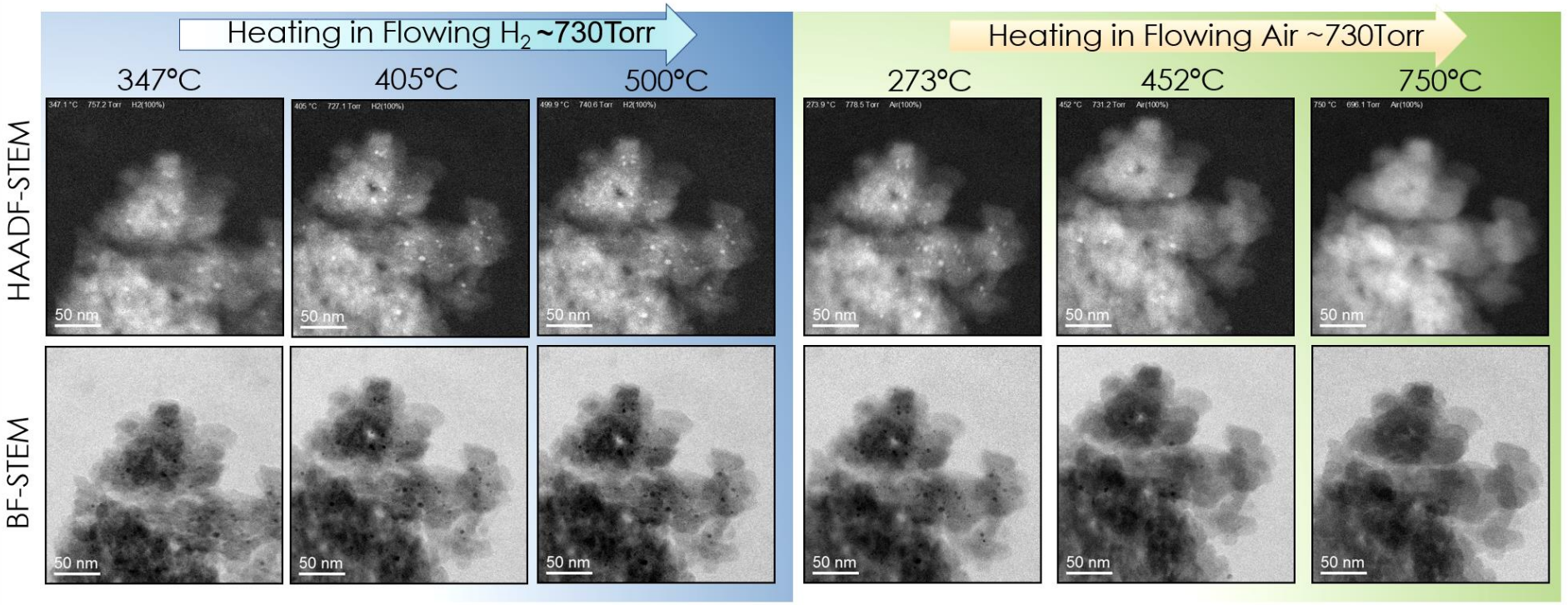




- H_2 TPR can differentiate ion-exchanged Pd from PdO particles and investigate speciation after various in-situ pretreatments.
- NH_4^+ back exchange can selectively titrate ion-exchanged Pd
- In as-prepared state, Pd does not exchange into CHA as efficiently as for BEA

In-situ STEM Characterization of Pd-BEA (Pd/Al = 0.09)

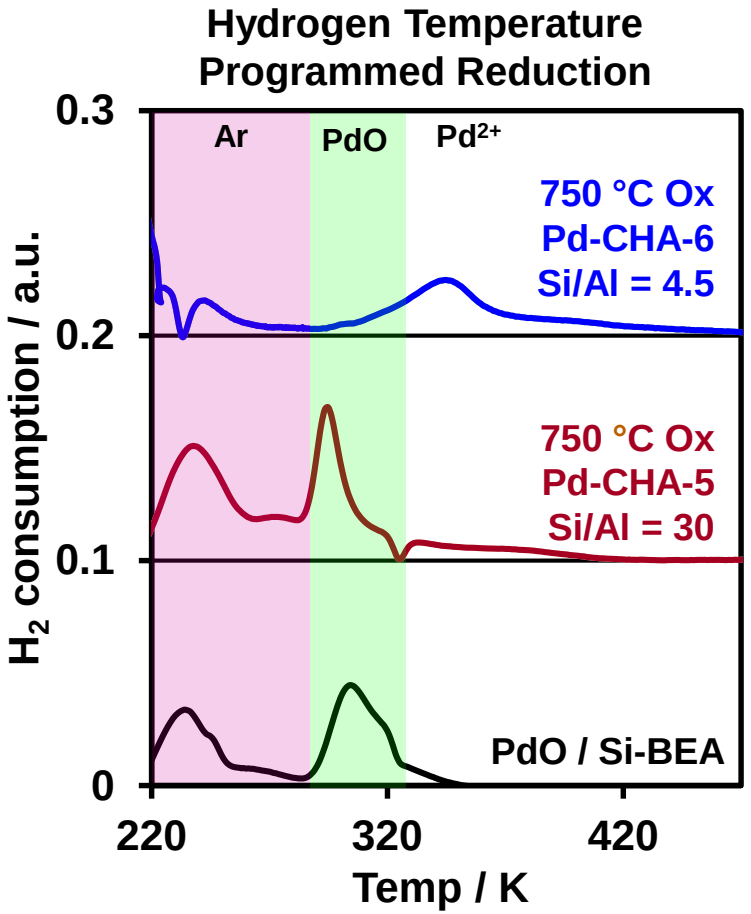
Ramp in H_2 → Switch to N_2 (20 Torr) → Cool to room temp. → Switch to air → Start heating

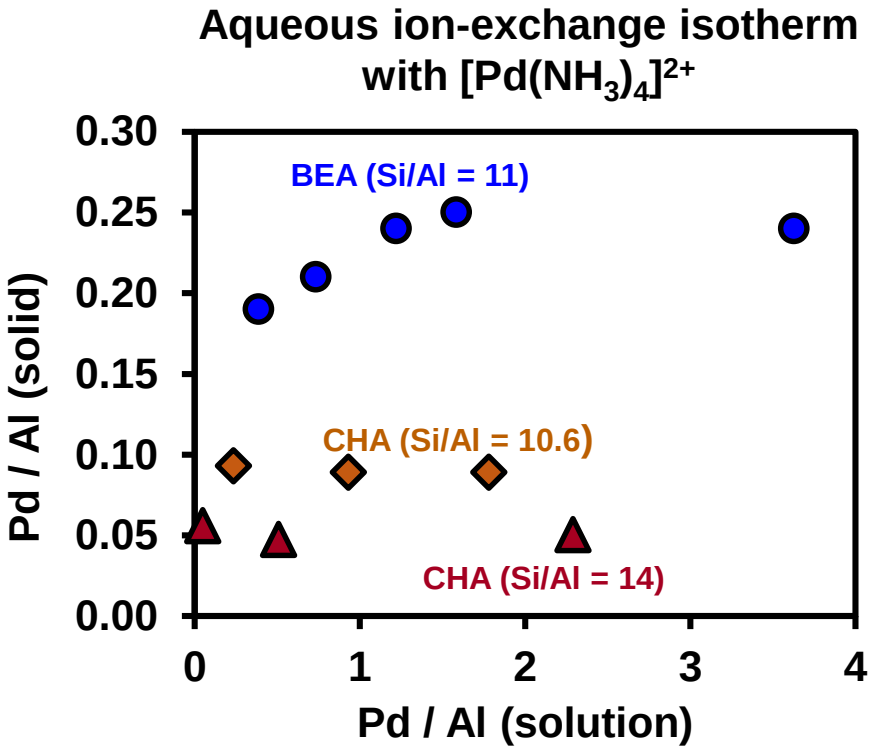


- **Increasing temperature in H_2 generates more and larger Pd particles**
- **Dry air treatments at 452 °C (Tamman temp. = 240 °C) are able to re-oxidize and re-disperse Pd**
- **At 750 °C in dry air, the majority of the PdO particles have re-dispersed**

Images and analysis courtesy of Dr. Unocic from ORNL

Al Site Requirements to Stabilize Ion-exchanged Pd^{2+}

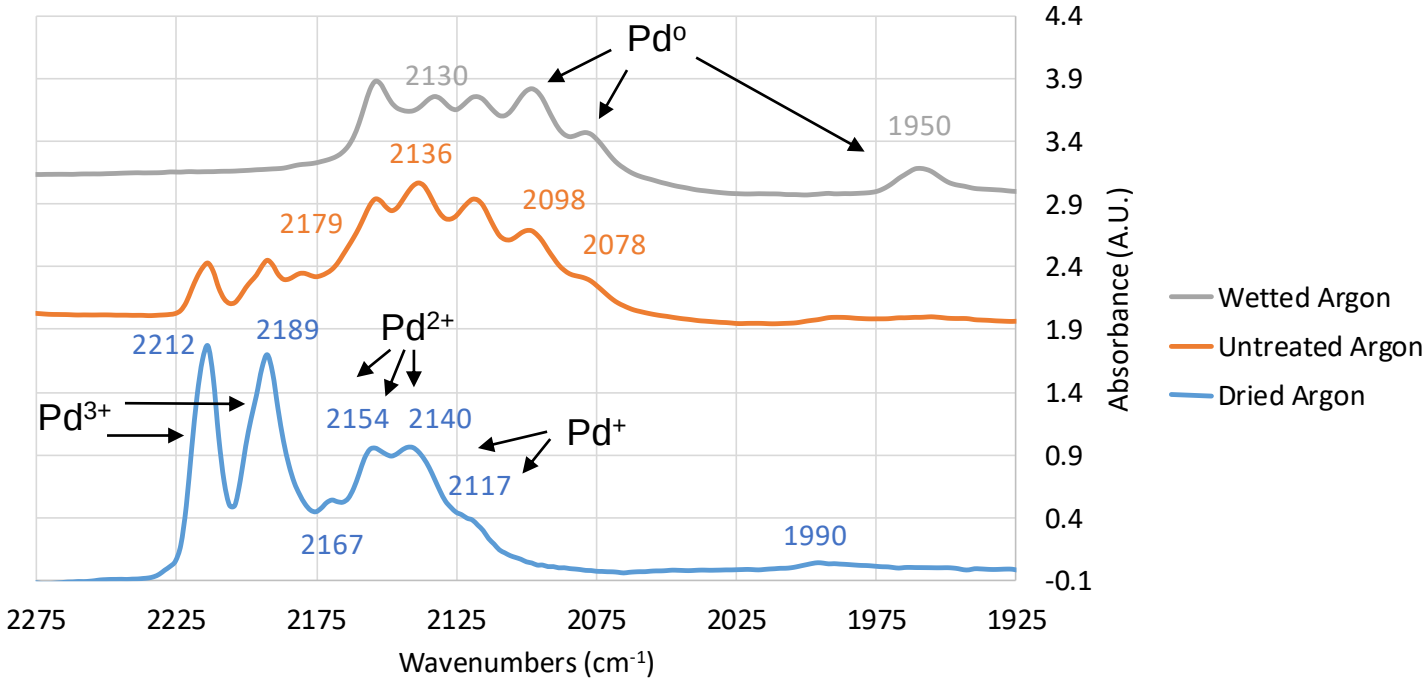




- As the Al density increases, so do the number of sites capable of stabilizing ion-exchanged Pd^{2+}
- Results suggest two, proximal Al sites are required for stabilizing ion-exchanged Pd^{2+}
- Dry oxidation treatments are capable of yielding predominately ion-exchanged CHA
- Proposed stable Pd species on zeolites are PdO and Pd^{2+} charge compensated by two Al sites

DRIFTS: Effect of Water on Palladium Speciation

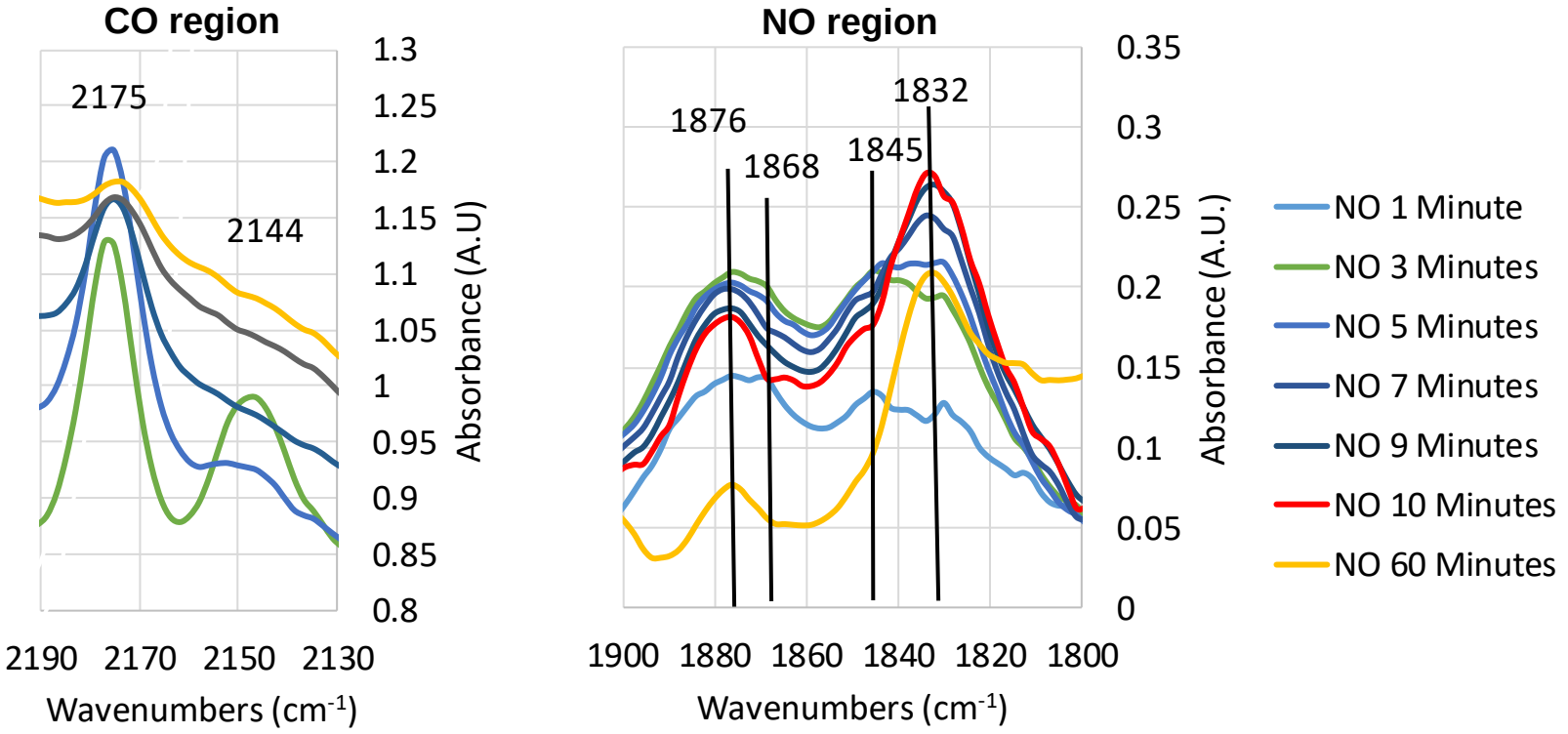
Pd-Beta treated in Ar at 500 °C, followed by CO adsorption at 25 °C



- **Presence of trace amount of water (<5 ppm in untreated argon) acts to reduce palladium at high temperatures; increasing water concentration leads to more intense Pd^0-CO bands (<2100 cm^{-1})**
- **Total elimination of trace water from the gas feed required to decouple effects of water from other gas species**

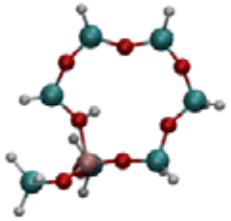
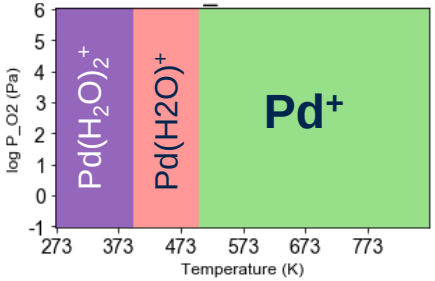
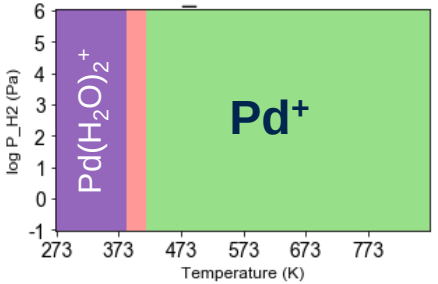
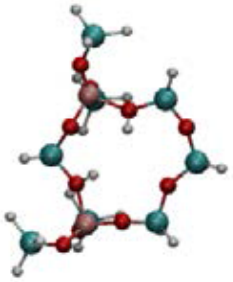
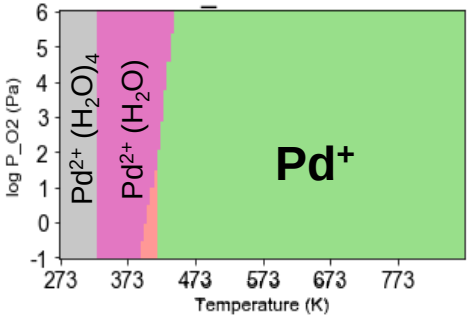
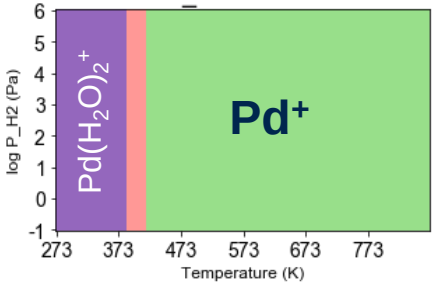
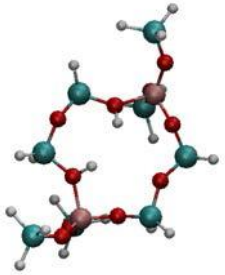
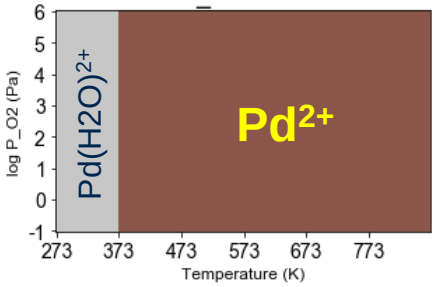
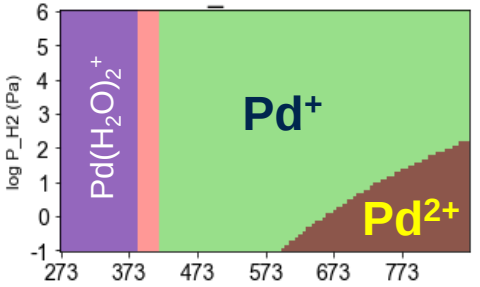
DRIFTS: CO Promotes NO Adsorption via Formation of $Pd(CO)(NO)^{n+}$ Complex

CO-NO Sequential Adsorption on Pd-Beta at 100 °C:



- **$Pd(CO)(NO)^{n+}$ species identified at 1868, 1845 cm^{-1} (N-O stretch) and 2175 cm^{-1} (C-O stretch)**
- **Co-adsorption features increase in intensity until 3-5 minutes then decrease; after 60 minutes NO exposure, only NO remains adsorbed**
- **NO readily displaces CO from catalyst surface at 100 °C**

Pd Speciation in CHA by QMMM DFT

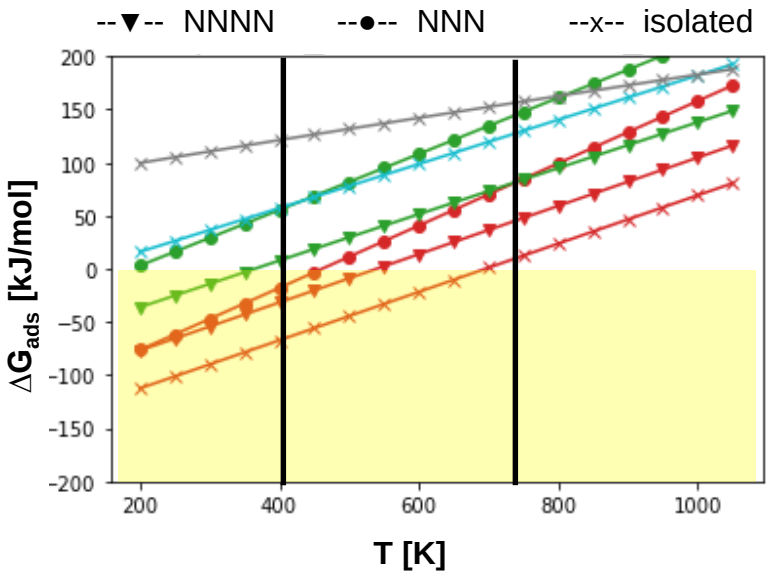
		wet, oxidizing feed	wet, reducing feed
Isolated Al			
NNN Al pair			
NNNN Al pair			

Unusual Pd^{+} species is predicted to be most stable over a wide range of oxidizing and reducing conditions

Computational Study of NO Adsorption

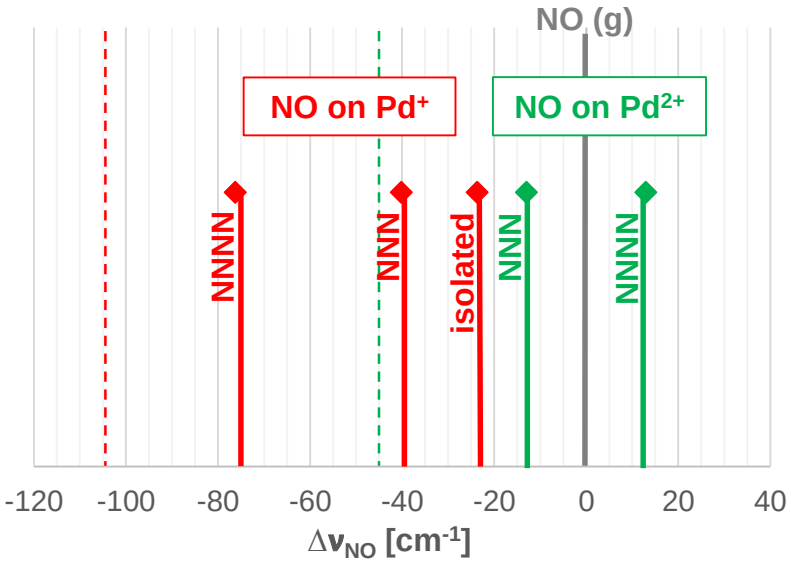
After pretreatment (air + 5% H_2O; 750 °C),
Pd^+ at isolated Al and NNN pairs
Pd^{2+} at NNNN pairs

Does NO adsorb on these sites?
→ ΔG_{ads} ; P_{NO} = 20 Pa



- NO adsorbs on **Pd^+** (desorption consistent with high T peak in TPD)
- NO does not adsorb on **Pd^{2+}**
- NO does not adsorb on **H^+**

Additional characterization:
IR stretching frequencies
(relative to gaseous NO)



- **Calculated NO stretch frequencies vary depending on specific configuration**
- **NO on Pd^+ stretches appear in region where peaks are observed experimentally (1800 – 1860 cm^{-1})**

Responses to Previous Year Reviewers' Comments

- Project was not reviewed last year

Remaining Challenges and Barriers

- Understanding the exposure conditions and mechanisms for Pd mobility in zeolites (Pd sintering, Pd re-dispersion, nature of mobile Pd species)
- Identifying the framework Al sites (e.g., proximal or isolated Al) required for stabilizing ion-exchanged Pd
- Identifying the adsorption sites corresponding to different forms of adsorbed NO observed during temperature programmed desorption
- Ascertaining the role – if any – of Pd nanoparticles and PdO clusters, inside CHA cage or on external zeolite surface
- Ascertaining whether Pd^{2+} sites undergo partial reduction in situ to enable NO adsorption. Is this facilitated by the presence of CO and/or HC?
- Degradation upon extended cycling is a major barrier to practical implementation

Future Work

On-going

- Determine the dependence of ion-exchanged Pd site number and structure on the framework Al arrangement in CHA zeolites
- More accurate calculation of IR features (frequencies + intensities) for comparison with DRIFTS experiments
- In-situ STEM analysis of Pd/zeolites under different catalyst pre-treatment conditions to aid in the interpretation of DRIFTS and XANES spectra
- Effect of CO and HC on NO adsorption: activation of Pd sites through partial reduction (e.g., to Pd^{+}) or chemical reaction with NO (e.g., formation of NCO species)?

Planned

- Explore whether viable reactivation strategies exist for recovering or even preventing catalyst degradation
- Explore how framework type, SAR, Al distribution impact NOx storage capacity and durability
- Monolithic Pd/zeolite catalyst performance evaluations in engine exhaust

Any proposed future work is subject to change based on funding levels

Summary

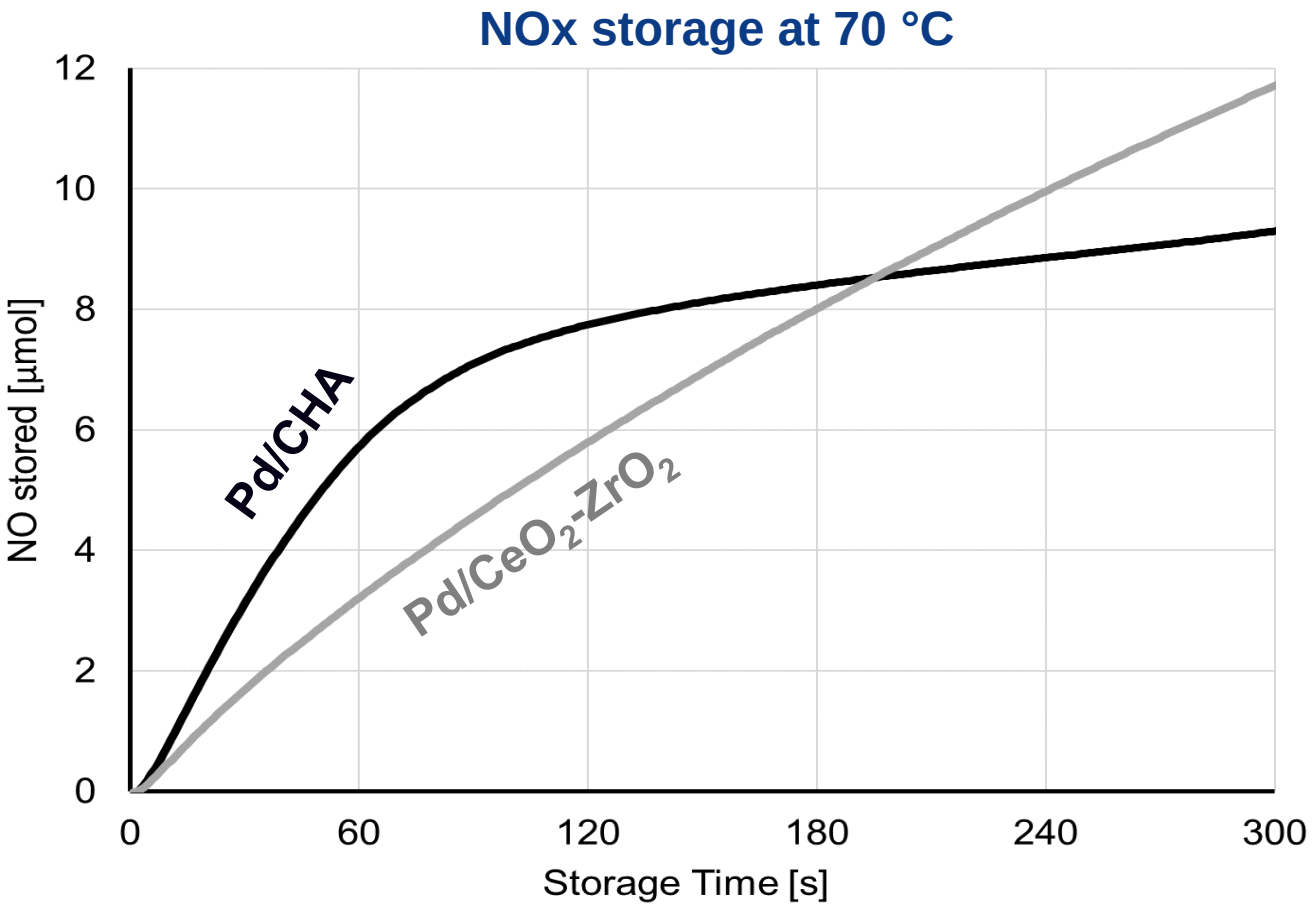
- Quantification of ion-exchanged Pd fraction by different techniques
- Increasing the bulk Al density in the zeolite results in higher amount of sites able to stabilize ion-exchanged Pd species, most likely two proximal aluminum sites
- Isolated Pd^{n+} species are essential for NO adsorption, and not metallic Pd/PdO
- Phase diagrams show that ionically dispersed Pd^{+} or Pd^{2+} is most thermodynamically preferred under a wide range of conditions
- Stability of Pd^{2+} at Al pair sites depends strongly on Al spacing
- Pd^{+} is identified as potential high-temperature NO adsorption site, Pd^{2+} appears unable to bind NO
- Pd/CHA is more effective for NOx storage than Pd/BEA or Pd/CeO_2-ZrO_2 in both lean (Diesel) and stoichiometric (gasoline) model exhaust feeds
- NOx storage on Pd/CHA is almost independent of oxygen level, but storage efficiency and release profile depend on the presence of reducing species
- NOx storage is repeatable across several tests, but degrades significantly during extended cycling

Technical Back-Up Slides

Milestones for FY2020

Task	Date	FY2020 Milestone Description	Status
Reactor studies	2/28/20	Steady state kinetics of NO reduction by C_2H_4 and CO determined for Pd/CHA and Pd/BEA	To be done
Catalyst characterization	5/31/20	Structure-property relations between Pd site types, spectroscopic features, and NO/HC adsorption behavior elucidated	To be done
Reactor studies	8/31/20	Cold start performance of Pd/CHA and Pd/BEA evaluated under simulated stoich. gasoline, lean burn gasoline and diesel exhaust	To be done
Computational studies	11/30/20	Energy and free energy landscapes for reactions of coadsorbed NO/CO, NO/ C_2H_4, & NO/$CH_3C_6H_5$ derived for Pd/CHA and Pd/BEA	To be done
Catalyst aging studies	11/30/20	Mechanism of Pd/zeolite catalyst degradation under hydrothermal aging elucidated	To be done
Prediction of vehicle performance	11/30/20	Impact of new catalyst on tailpipe emissions estimated using vehicle emission model	To be done
Catalyst performance validation (Go/no-go)	11/30/20	Optimized HC/NO adsorber catalyst validated using engine exhaust: NO adsorption and high temperature retention (up to 300 °C) superior to Pd/CeO_2-ZrO_2 after 50 h 4-mode aging	To be done

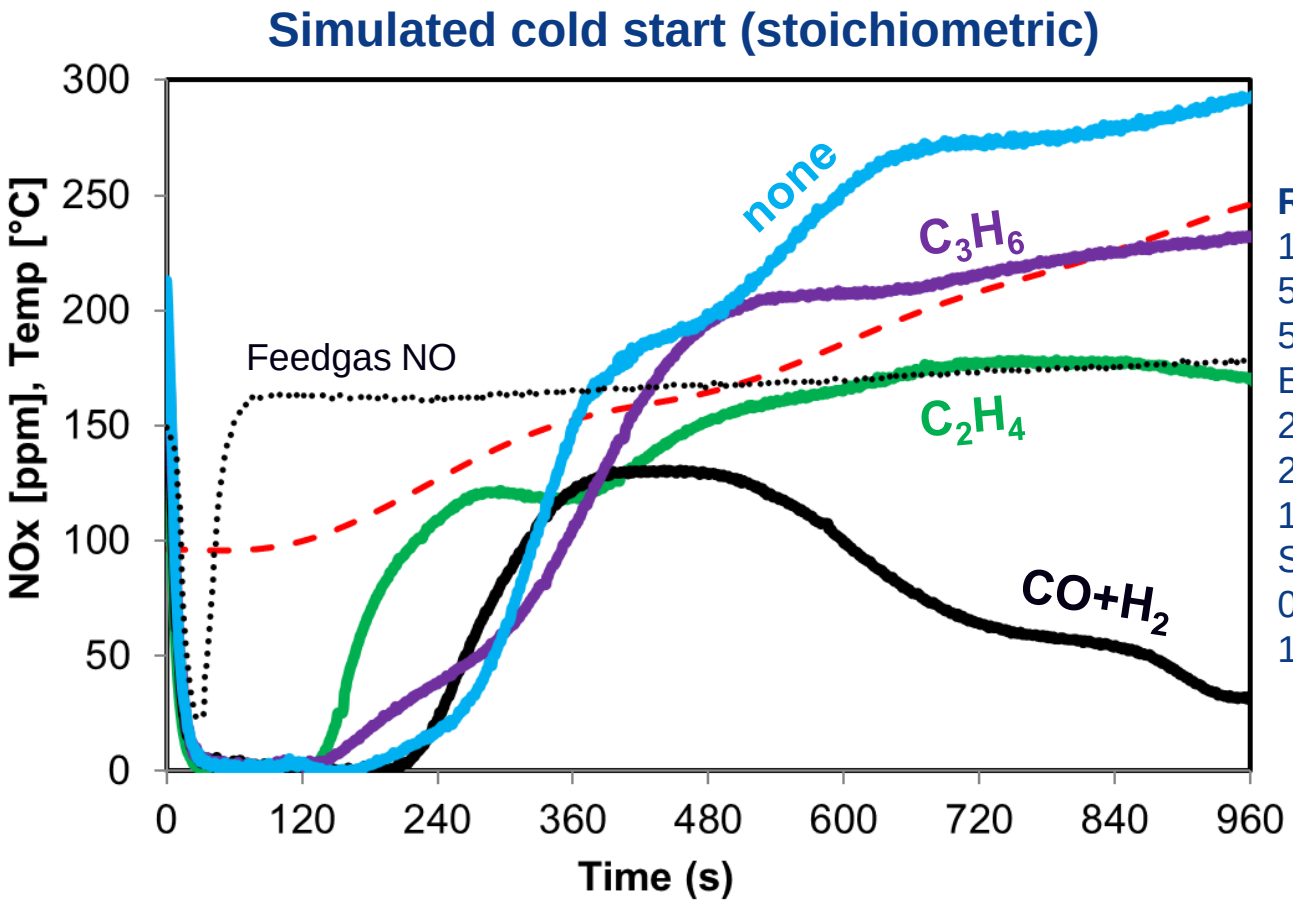
Comparing PNA Technologies (stoichiometric)



0.10% O_2
2% H_2O
500 ppm CO
100 ppm C_3H_6
100 ppm C_2H_4
100 ppm NO

Initial storage efficiency of Pd/CHA is almost double that of Pd/CeO_2-ZrO_2

Pd/CHA: Effect of Reductant on NO_x Storage



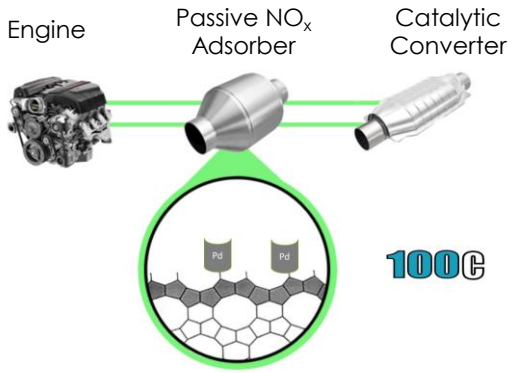
Ramp from 90 °C
170 ppm NO
5% H_2O
5% CO_2
Either no reductant, or
200 ppm C_3H_6, or
250 ppm C_2H_4, or
1350 ppm CO + 450 ppm H_2
Stoich. level of O_2
0.8 g powder
1.2 L/min total flow

NO_x storage and conversion highest with $CO+H_2$, lowest with C_2H_4

Reactor studies of NO/HC adsorption

Objective

- Optimize adsorption conditions to achieve high uptake of NO
- Investigate the effects of varying these conditions and other co-feed chemicals (e.g. C_2H_4, CO, etc.)



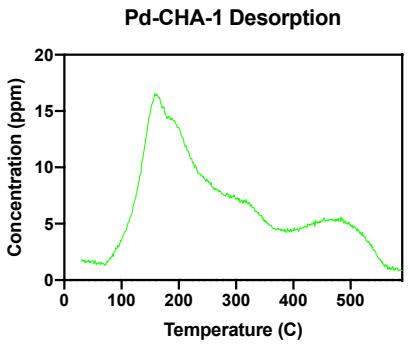
Methodology

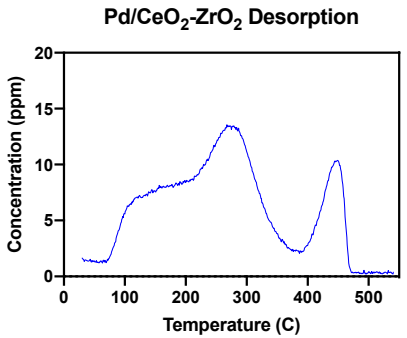
- **Pretreatment:** feed air (20% O_2) and 5% H_2O, and heat sample to 750ºC for five hours
- **Adsorption:** at selected adsorption temperature (typically 75ºC), feed ~200 ppm NO in He and 1% CH_4 as tracer
- **Desorption:** run temperature-programmed desorption, and heat catalyst to 500ºC in He flow at 10ºC/min
- **Post treatment:** regenerate adsorption sites by flowing a mix of He, air, and H_2O

Key Findings

Adsorption capacity of Pd-CHA-1 larger than that of PNA standard (Pd/CeO_2-ZrO_2) under feed of NO in He

Catalyst	NO/Pd Adsorption	NO/Pd Desorption
Pd-CHA-1	0.11	0.11
Pd/CeO_2-ZrO_2	0.06	0.09

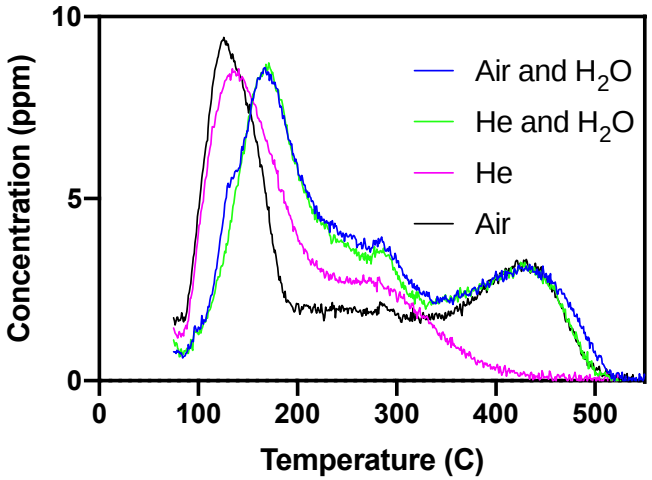




Reactor studies of NO/HC adsorption

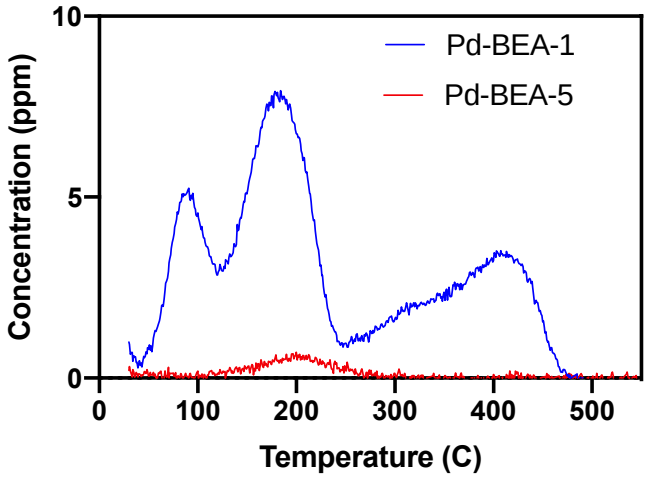
Key Findings (continued)

Desorption - Effect of Post Treatment



- O_2 in air is sufficient to regenerate most NO adsorption sites but H_2O is essential to fully regenerate the high-temperature sites of Pd-CHA-1.

Desorption - Effect of isolated Pd



Catalyst	NO/Pd Adsorption	NO/Pd Desorption
Pd-BEA-1	0.02	0.02
Pd-BEA-5	0.001	0.001

- For Pd-BEA-1, Pd_{iso}/Pd_{total} = 0.79 (after 200ºC pretreatment). For Pd-BEA-5, Pd_{iso}/Pd_{total} = 0.03, suggesting that isolated Pd sites are more important for NO adsorption than Pd nanoparticles or PdO clusters.
- Also, the fraction of NO desorbing from the high temperature site (around 400ºC) are the same for both the Pd-CHA-1 and Pd-BEA-1 samples – suggests that they share the same site/state of Pd.

Future Steps

Investigate the adsorption of C_2H_4 and the effect of co-feeding on NO adsorption.